Benchmarking correlated methods for frequency dependent polarizabilities: aromatic molecules with the CC3, CCSD, CC2 and SOPPA methods

Jørgensen, Maria West; Faber, Rasmus; Ligabue, Andrea; Sauer, Stephan P. A.

Publication date:
2019

Document version
Other version

Benchmarking correlated methods for frequency dependent polarizabilities: aromatic molecules with the CC3, CCSD, CC2 and SOPPA methods

Maria W. Jørgensen, Rasmus Faber, Andrea Ligabue, Stephan P. A. Sauer*

Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

June 7th 2019

Abstract

A benchmark of different correlated second-order methods for frequency dependent polarizabilities has been carried out. For the benchmark a set of 15 (hetero-)aromatic medium sized molecules has been optimized at MP2/6-31G(d) level. For the first time CC3 polarizabilities are reported for these molecules using Sadlej's polarized triple zeta basis set and for a subset of these molecules the polarizabilities were obtained at the CC3 level also with the larger aug-cc-pVTZ basis set. These CC3 values are used as the reference values for benchmarking the second-order methods. The influence of different basis sets; aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, d-aug-cc-pVTZ, Sadlej, on static and frequency dependent polarizabilities were tested for the set of molecules at the SOPPA level. It was found that, though not much, the basis sets had a greater influence on the frequency dependent polarizabilities than on the static ones. The aug-cc-pVTZ basis set performed adequately for both static and frequency dependent polarizabilities having an insignificant off-set from the values obtained with the larger aug-cc-pVQZ basis set. Further more Sadlej's basis set was also found to give reliable results. Comparing the second-order methods; SOPPA, SOPPA(CC2), SOPPA(CCSD), CC2 and CCSD to the CC3 reference values, it was found that the best performing method was the CCSD, as expected. The faster SOPPA method, however, outperformed CC2, suggesting the use of SOPPA rather than CC2 for polarizabilities. The SOPPA results were found to improve further, when the correlation coefficients in the wavefunction were replaced by coupled cluster amplitudes in the SOPPA(CC2) and SOPPA(CCSD) methods. A comparison was made, for a small set of the molecules, between experimental data and calculated polarizabilities. It shows that, for this set of molecules, the trend for the performances of the different second-order methods does not change whether the reference values are calculated CC3 values or experimental values.

Keywords: Frequency dependent polarizabilities, basis set dependence, CC3, SOPPA, SOPPA(CC2), SOPPA(CCSD), CC2, CCSD